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## Structural characterization of palladium-platinum particles in natural-gas-oxidation catalyst – Ex-situ and preliminary in-situ thermal aging studies

Mari Honkanen<sup>1\*</sup>, Marja Kärkkäinen<sup>2</sup>, Tanja Kolli<sup>2</sup>, Olli Heikkinen<sup>3</sup>, Kauko Kallinen<sup>4</sup>, Jakob Birkedal Wagner<sup>5</sup>, Thomas Willum Hansen<sup>5</sup>, Diego Gardini<sup>5</sup>, Mika Huuhtanen<sup>2</sup>, Riitta L. Keiski<sup>2</sup>, Jouko Lahtinen<sup>3</sup>, Minnamari Vippola<sup>1</sup>

*1 – Department of Materials Science, Tampere University of Technology, P.O.B. 589, 33101 Tampere, Finland*

*2 – Environmental and Chemical Engineering, Faculty of Technology, University of Oulu, P.O.B. 4300 Oulu, Finland*

*3 – Department of Applied Physics, Aalto University, P.O.B. 14100, 00076 Aalto, Finland*

*4 – Dinex Ecocat Oy, Typpitie 1, 90620 Oulu, Finland*

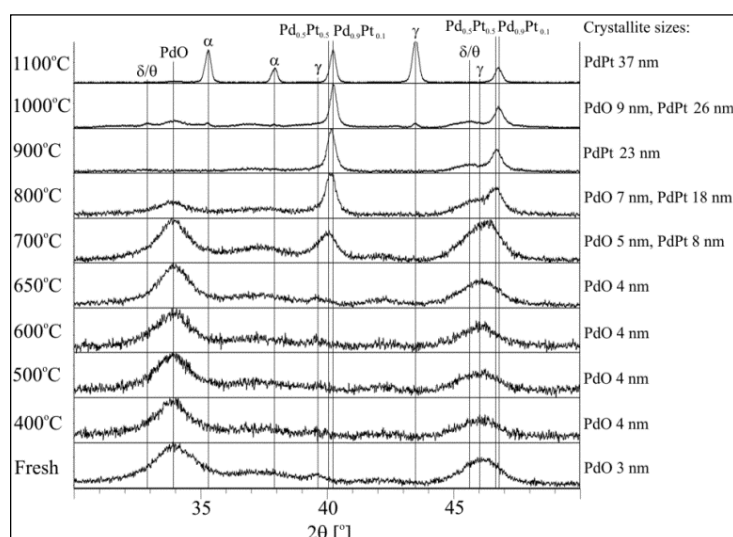
*5 – Center for Electron Nanoscopy, Technical University of Denmark, Fysikvej, 2800 Kgs. Lyngby, Denmark*

*\* corresponding author's email: mari.honkanen@tut.fi*

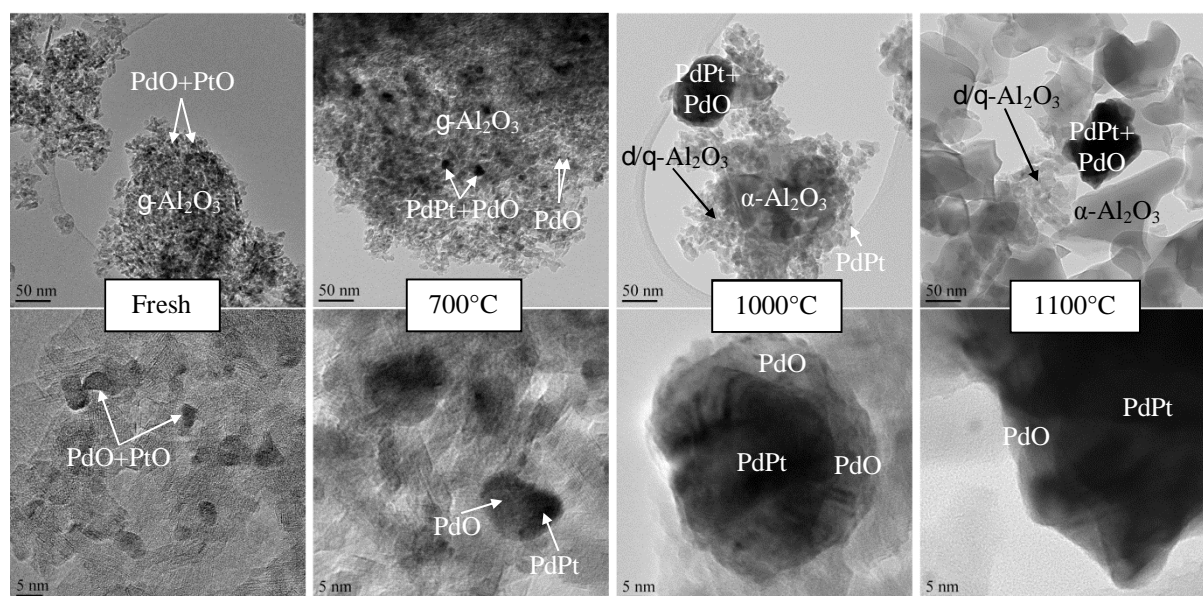
Natural gas (NG) is a potential sustainable energy source for vehicles because exhaust emissions from NG engines are much lower than those from e.g. diesel engines. Worldwide, there are more than 17 million NG-powered vehicles and recently a total amount of NG vehicles (NGVs) has increased exponentially [1]. Exhaust gases of NGVs contain, however, unburned methane which is a potential greenhouse gas and ozone precursor. EU emission standards have regulated CH<sub>4</sub> emissions from new NG-heavy-duty vehicles since 2000 [2]. To fulfill all the time tightening regulations and to achieve a clean atmosphere, a strong effort to further develop efficient and resistant catalysts for NGVs is required. Supported palladium catalysts are known to be active for methane combustion. However, their deactivation, caused by poisoning and thermal aging, is a problem. It is well-known that methane oxidation activity of the Pd-catalysts decreases e.g. when PdO composes to metallic and when PdO particles sinter at elevated temperatures. The aim of this work was to study the structural changes of noble metal particles in the PtPd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> natural-gas-oxidation catalyst at elevated temperatures. Changes compared to the fresh catalyst were studied ex-situ by various characterization methods. Changes were studied also in-situ by environmental transmission electron microscope (ETEM).

The ex-situ thermal aging treatments were carried out at various temperatures between 400–1100°C for 5 hours in oxidative (80% N<sub>2</sub> + 20% O<sub>2</sub>) and in reductive (95.5% N<sub>2</sub> + 0.5% O<sub>2</sub>) atmospheres. Before and after the treatments, the catalyst was characterized by X-ray diffractometer (XRD) and analytical transmission electron microscope (TEM). Specific surface area, pore size, and pore volume as well as surface characteristics by X-ray photoelectron spectroscopy (XPS) were determined for the fresh and selected heat-treated catalysts. The in-situ studies were carried out with ETEM by heating the fresh catalyst sample from room temperature up to 900°C.

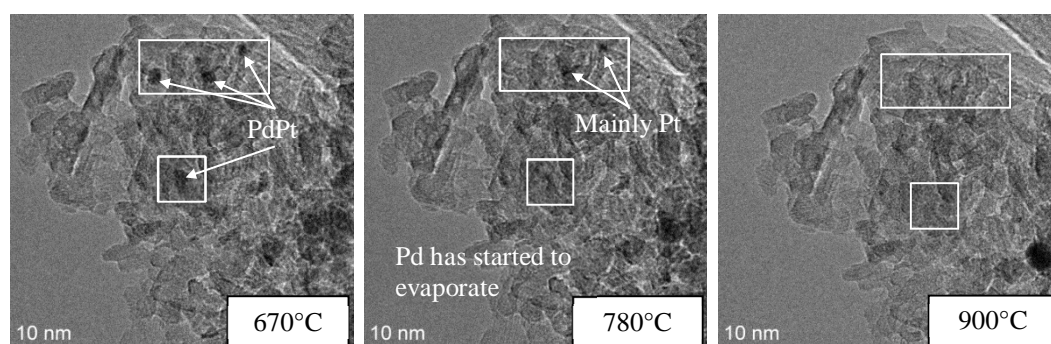
The fresh catalyst consists of small (<5 nm) and well-distributed PtPd (1:4 wt%) particles in the oxide form on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Figs. 1 and 2) with high specific surface area. Thermal aging treatments caused significant structural changes in the catalyst, however, critical temperature levels were above the normal exhaust gas temperature (<500°C) of the NG-oxidation catalyst [3]. According to the ex-situ studies in the oxidative atmosphere, the first changes in the noble metal particles were detected after the thermal aging treatment at 700°C (Fig. 1). Slightly grown particles formed and they seemed to have a PdPt core and a PdO shell, also small PdO particles were still detected (Fig. 2). In addition, specific surface area of the catalyst decreased slightly. Phase transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\delta$ - and/or  $\eta$ -Al<sub>2</sub>O<sub>3</sub> was detected after the treatment at 800°C (Fig. 1). More changes after the treatment at 1000°C were observed (Figs. 1 and 2); core-shell noble metal particles had grown still, however, also small metallic PdPt particles were detected. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was changed to  $\delta$ - and/or  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and also  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was observed. Specific surface area was significantly decreased compared to the fresh catalyst. In the treatment at 1100°C, large bimetallic PtPd particles with a thin PdO shell formed, in addition, the support transformed mainly to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Figs. 1 and 2). Specific surface area and total pore volume collapsed. In the in-situ studies, structural changes in the catalyst sample could be followed in the real time. However based on our preliminary studies, it is very challenging. In the high vacuum,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was very beam and temperature sensitive.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> could be stabilized by drying the sample in the ETEM at 130°C in high vacuum for few minutes. However, the problem was evaporation of Pd at temperatures above 700°C (300 Pa O<sub>2</sub>). Thus, the size of the particles reduced instead of sintering and mainly Pt was detected in the particles (Fig. 3).



**Figure 1.** XRD patterns and average crystallite sizes of the noble metal particles for the fresh and heat-treated catalysts



**Figure 2.** TEM images of the fresh catalyst and the catalyst after thermal aging at selected temperatures



**Figure 3.** ETEM images of the catalyst at selected temperatures in 300 Pa O<sub>2</sub>

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